

A P P L I C A T I O N

Atty Docket: 10270/37C

TO THE HONORABLE COMMISSIONER OF PATENTS:

Be it known that **ASLAM A. MALIK** a citizen of the United States and resident of Cameron Park, County of Sacramento, State of California; **GERALD E. MANSER** a citizen of the United States and resident of El Dorado Hills, County of El Dorado, State of California; **THOMAS G. ARCHIBALD** a citizen of the United States and resident of Fair Oaks, County of Sacramento, State of California; **JETTY L. DUFFY-MATZNER** a citizen of the United States and resident of Davis, County of Yolo, State of California; **WILLIAM L. HARVEY** a citizen of the United States and resident of Carmichael, County of Sacramento, State of California; **GARY J. GRECH** a citizen of the United States and resident of Carmichael, County of Sacramento, State of California; **ROLAND P. CARLSON** a citizen of the United States and resident of Folsom, County of Sacramento, State of California, have invented new and useful improvements in:

**MONO-SUBSTITUTED FLUORINATED OXETANE MONOMERS AND PREPOLYMERS, AND
METHODS OF PREPARATION AND POLYMERIZATION TO PRODUCE FLUORINATED
ELASTOMERS**

of which the following is a specification.

SPECIFICATION

CROSS REFERENCE TO RELATED APPLICATIONS:

This application is a Continuation-In-Part application of our copending application SN 08/206,859, filed March 7, 1994, which in turn is a Continuation application of SN 07/911,461, filed July 7, 1992, currently abandoned.

FIELD:

5 This invention relates to prepolymer compositions and the polymers derived therefrom, oxetane monomers having asymmetric mono-substituted pendant fluorinated alkoxymethylene groups as the prepolymer precursors, methods of preparing the precursor monomers and methods of polymerization of the prepolymers to form fluorinated
10 elastomers. The hydroxy-terminated prepolymers have a polyether backbone and are useful, inter alia, for the preparation of polyurethane elastomers, thermoset plastics and coatings. These compositions exhibit hydrophobic properties, very low surface energies, low glass transition temperatures, low di-electric constants, high abrasion resistance and tear strength, low
15 coefficient of friction, high adhesion and low refractive indices.

BACKGROUND:

15 Fluorinated Elastomers

Fluorinated polymers enjoy widespread use as hydrophobic, oleophobic coatings. These materials exhibit excellent environmental stability, high hydrophobicity, low surface energy and a low
20 coefficient of friction, and are used in a number of applications ranging from non-stick frying pans to optical fiber cladding.

Most fluoropolymers, however, are plastics that are difficult to process, difficult to apply and are unsuitable as coatings for flexible substrates due to their high rigidity. One example of a
25 widely used fluorinated material is Teflon, a

polytetrafluoroethylene. Teflon is difficult to process in that it is a rigid solid which must be sintered and machined into its final configuration. Commercial application of Teflon as a coating is complicated by its poor adhesion to a substrate and its inability to form a continuous film. As Teflon is insoluble, application of a Teflon film involves spreading a thin film of powdered Teflon onto the surface to be coated, and thereafter the powdered Teflon is sintered in place resulting in either an incomplete film or having many voids. As Teflon is a hard inflexible plastic, a further limitation is that the substrate surface must be rigid otherwise the Teflon will either crack or peel off.

A limited number of commercial fluoropolymers, such as Viton, possess elastomeric properties. However, these materials have relatively high surface energies (as compared to Teflon), poor abrasion resistance and tear strength, and their glass transition temperatures are still high enough ($>0^{\circ}\text{C}$ for Viton) to significantly limit their use in low temperature environments.

Accordingly there is a need for fluoroelastomers having hydrophobic properties, a surface energies and coefficients of friction at least equivalent to the fluorinated plastics (such as Teflon). Further, such fluoroelastomers must have high adhesion, high abrasion resistance and tear strength, low index of refraction and a low glass transition temperature so that it is suitable for any foreseeably low temperature environment use. Additionally, there is a need for fluoroelastomers that are easily produced in high yields and easy to use. Currently, there are no fluoroelastomers that satisfy all of these needs.

Premonomers

We have discovered and recognized that the conspicuous absence of fluorelastomers in the art exhibiting all of the above enumerated properties can be understood upon analysis of the upstream end of the current processes for synthesis of fluoropolymers and plastics. The kinds and properties of the premonomers currently used in turn result in the limitations in the properties of the monomers,

which further limit the diversity and properties of currently known fluoropolymers and fluoroelastomers.

5 It is known that a haloalkyl oxetane can be substituted in the 3-position with methyl groups containing energetic functional groups such as nitrate, azide, nitro and difluoroamino. The polymerization of these substituted oxetanes in the presence of polyhydroxy aliphatic compounds produces hydroxy-terminated prepolymers having a polyether backbone with pendant energetic groups.

10 The use of substituted oxetanes as a starting material for the production of polyethers is not new. However, the theme running through the art is that bis-substituted oxetanes are of primary interest and commercial importance. This is understandable in that the bis-haloalkyl oxetane starting material or premonomer is easily produced, whereas the mono-substituted 3-haloalkyl methyl oxetane premonomer is difficult and expensive to produce. There is little teaching in the art for guidance on easy, inexpensive methods of preparation of 3-haloalkyl-3-methyl (mono-substituted) oxetane premonomers or their use in synthesizing mono-substituted fluorinated oxetane monomers.

20 Bis-haloalkyl oxetane premonomers as a starting material are described in Falk et al. (U.S. 5,097,048). Falk disclose 3,3'-bis perfluoroalkyl oxetane monomers derived from bis-haloalkyl oxetane as a starting material. Reaction of the bis-haloalkyl oxetane with a perfluoroalkyl thiol, a perfluoroalkyl amine, a perfluoroalkanol, or 25 a perfluoroalkyl sulfonamide will produce the 3,3'-bis perfluoroalkyl oxetane monomer described in this reference.

30 Bis-haloalkyl oxetane premonomers are readily commercially available and their derivatives are fairly well covered in the art. Mono-haloalkyl oxetanes, however, are rarely mentioned in the art, appearing only as an incidental comparison in a more complete investigation of the bis-haloalkyl oxetanes. The lack of teaching regarding the mono-substituted fluorinated alkoxymethylene oxetanes (herein "FOX" compounds for Fluorinated Oxetane), and their relative 35 commercial unavailability, is undoubtedly due to the fact that mono-

substituted haloalkyl oxetanes are very difficult and expensive to make. Current processes for the production of mono-substituted haloalkyl oxetane premonomers, such as 3-bromomethyl-3-methyloxetane ("BrMMO"), are typified by low yields, long, complicated synthetic schemes and the use of toxic, expensive chemicals to convert 1,1,1-tris(hydroxymethyl)ethane ("TME") into BrMMO.

In these processes, TME is reacted with diethyl carbonate to produce the corresponding cyclic carbonate. This in turn undergoes decarboxylation upon thermal decomposition at 160 °C to provide 3-hydroxymethyl-3-methyloxetane ("HMMO"). The HMMO is converted to the primary chloro compound with carbon tetrachloride and triphenyl phosphine. Reaction of the chloro compound with sodium bromide in methyl ethyl ketone results in S_N2 displacement of the chlorine to produce BrMMO. This scheme is commercially impractical in that it is both labor intensive and requires expensive, toxic chemicals. Consequently, these disadvantages have precluded the use of mono-substituted fluorinated oxetane (FOX) monomers that may be derived from mono-substituted haloalkyl oxetanes, such as BrMMO, and production of polymer products thereof.

Accordingly, there is a need for a mono-substituted fluorinated alkoxymethylene oxetane monomer with a fluorinated side-chain capable of producing prepolymers and polymers having desirable properties, such as oil and water repellency, at least comparable to the bis-substituted perfluoroalkyl oxetanes known in the literature. Further, there is also a need for a high yielding reaction pathway for production of the mono-substituted haloalkyl premonomer, characterized by a minimum production of by-products, and a commercial feasibility for high volume, high yield production without the excessive labor and materials costs associated with the currently known processes.

Monomers and Prepolymers

The most important criteria in the development of release (i.e., non-stick), high lubricity coatings is the minimization of the free surface energy of the coating. Free surface energy is a measure

of the wettability of the coating and defines certain critical properties, such as hydrophobicity and adhesive characteristics of the material. For most polymeric surfaces the surface energy (dispersion component) can be expressed in terms of the critical surface tension of wetting γ_c . For example, the surface energy of Teflon (represented by γ_c) is 18.5 ergs/cm², whereas that of polyethylene is 31 ergs/cm². Consequently, coatings derived from Teflon are more hydrophobic and non-stick than those derived from polyethylene. A substantial amount of work has been done by the coating industry to develop coatings with surface energies lower than or comparable to Teflon while at the same time exhibiting superior adhesion characteristics.

The literature teaches that in order to prepare coatings with the desirable low surface energy, the surface of the coating must be dominated by -CF₃ groups. Groups such as -CF₂-H and -CFH₂ increase the surface energy of the material. The importance of the number of fluorine atoms in the terminal group (i.e., the group present on the surface) was demonstrated in Zisman et al., *J. Phys. Chem.*, 1953, 57, 622; *ibid. J. Colloid Sci.*, 1954, 58, 236; Pittman et al., *J. Polymer Sci.*, 1968, 6, 1729. Materials with terminal -CF₃ groups exhibited surface energies in the neighborhood of 6 ergs/cm², whereas similar materials with terminal -CF₂H groups exhibited values in the neighborhood of 15 ergs/cm², more than twice the value for the material with terminal -CF₃ groups. Teflon incorporates the fluorine moieties on the polymer backbone and does not contain pendant -CF₃ groups. Consequently, Teflon does not exhibit surface energies as low as polymers having terminal perfluorinated alkyl side-chains.

A critical requirement in the production of an elastomer is that the elastomer have large zones, or "soft segments", where little or no crosslinking occurs and where the polymer conformation is such that there is little or no compaction of the polymer as a result of crystallization. Intermediate of these soft zones are "hard blocks" wherein there may be significant hydrogen bonding, crosslinking and compaction of the polymer. It is this alternating soft block and hard block which gives the polymer its elastomeric properties. The

longer the soft segment, the more elastic the elastomer.

We have discovered that an improved route to producing elastomers is to produce homo- or co-prepolymers characterized as non-cross linked, assymetrical, hydroxy-terminated, linear oligomers having from about 10 to about 500 carbons, preferrably 20 to about 200 carbons. These prepolymers substantially retain their integrity in subsequent polymerizing reactions to provide the soft segment zones of the resulting polymers which, in combination with the hard blocks formed during polymerization, produce good elastomers. We have found that the literature does not have any showing of homo- or co-polymerization of either the bis or the mono-substituted fluorinated alkoxyethylene oxetanes to produce soft segment containing prepolymers required for production of elastomers. Accordingly, there is a need for fluorinated oxetane (FOX) monomers having a side-chain with an omega or terminal perfluorinated alkyl group, which monomers are capable of homo-polymerization or copolymerization to produce the soft segment, herein "FOX prepolymers", necessary for a fluorinated elastomer.

Further, in order for the hydroxy-terminated prepolymer with a fluorinated side-chain (i.e., FOX prepolymers) to be useful, it must have a functionality of at least 2. Presence of non-functional or mono-functional materials in the prepolymers result in coatings with poor mechanical and surface properties. Consequently, these coatings have limited commercial value. Non-functional materials, mainly cyclic tetramers and trimers, are formed during the ring opening polymerization from chain "back-biting". Monofunctional materials, on the other hand are formed due to counter-ion terminations, such as diethyl ether and fluoride ion terminations.

Falk et al. (US 5,097,048) disclose the synthesis of bis-substituted perfluoroalkyl oxetane monomer from bis-haloalkyl oxetane, the perfluoroalkyl glycols derived therefrom, including related thiol and amine linked glycols and dimer diols. Most of the fluorinated side-chains are attached to the glycol unit by either a thio, an amine or a sulfonamide linkage. Only a few of their examples describe glycols with fluorinated alkoxyethylene side-

chains.

Falk et al. (EP 03 48 350) report that their process yields perfluoroalkyloxymethylene neopentyl glycols composed of a mixture of (1) approximately 64% of the bis-substituted perfluoroalkyl neopentyl glycol, and (2) approximately 36% of a mono-substituted perfluoroalkyl neopentyl glycol product with a pendant chloromethyl group. Evidently, the mono-substituted product results from incomplete substitution of the second chloride on the bis-chloroalkyl oxetane starting material. Consequently, as noted from the Zisman and Pittman work above, the presence of the $-CH_2Cl$ as a side-chain significantly increases the surface energy of coatings made from these polymers thus reducing the hydrophobicity and oleophobicity of the coating.

Not surprisingly, it is understandable that Falk et al. (US 5,097,048) discourages the use of the mono-substituted glycol for the preparation of low surface energy coatings, since the monosubstituted glycol as produced from bis-chloroalkyl oxetanes would necessarily have a residual chloromethyl group still attached to the 3-carbon because of the incomplete substitution of the bis-haloalkyl moieties on the starting material. Accordingly, their teaching that the polymer derivatives from mono-substituted glycols do not produce a coating exhibiting the desired properties, as compared to coatings derived from bis-substituted glycols, is a direct result of the increase in free energy associated with the remaining chloromethyl group on Falk's mono-substituted glycol.

Moreover, the reference cited by Falk et al. in the '048 patent, J. Org. Chem., 45 (19) 3930 (1980), stating at line 33 that "mono-fluoroalkyl oxetanes containing oxygen have been reported" is misleading in that the reference cited discusses oxetanes substituted with $-CH_2F$ side chains (i.e., (monofluoro)alkyl oxetanes) and not alkoxyethylene side chains with terminal prefluoroalkyl groups. Hence, this reference will not lead to materials with low surface energies and is not relevant to the compounds of this invention.

Falk et al. (US 5,097,048) teaches preparation of dimers with fluorinated side-chains having thio linkages, but not of dimers with

fluorinated ether side-chains. This is because his synthesis route for preparing dimers with thio linkages cannot be used for the synthesis of dimers with ether linkages. In other words, Falk et al. does not teach preparation of long chain polyethers with fluorinated ether side-chains.

Falk et al. (US 4,898,981) teaches incorporation of their bis-substituted glycols into various foams and coatings to impart to them the desired hydrophobicity and oleophobicity. Classic polyurethane chemistry shows that while a plastic may form by reaction of Falk's glycols with the diisocyanates, elastomers can not form since there is no long chain soft segment. As noted above, such a soft segment is needed for the formation of an elastomer. Since the Falk et al. compounds are only one or two monomer units long, it is clearly too short to function as a soft segment for the formation of a polyurethane elastomer. In Falk et al., the fluorinated glycol and isocyanate segments alternate, with the fluorinated glycol segments being nearly the same size as the isocyanate segments. It is well known that such a polymer structure will not yield elastomers.

None of the Falk et al. references teach or show a homopolymer or co-prepolymer made from bis-perfluoroalkoxymethylene oxetanes, nor polyurethanes derived therefrom or from the corresponding glycols. All of their polyurethanes are made directly from the thiol linked monomers and dimers and not via a prepolymer intermediate. In the examples provided in Falk et al. (US 5,097,048), particularly where the fluorinated side-chains are large and for all of the dimers, all have thiol linkages; no ether side-chains are shown. The polyurethanes disclosed by Falk et al. (US 4,898,981) are made from the perfluoroalkylthio neopentyl glycol. They do not teach, show or suggest producing a polyurethane from the perfluoroalkoxy neopentyl glycol monomer, nor do they suggest, teach or show the types of prepolymers and polymers that can be prepared from the mono-substituted 3-perfluoroalkoxymethylene-3-methyl oxetanes (i.e., FOX monomers). However, Falk et al. (US 5,097,048) in their Example 12 show a polyether prepolymer prepared from a bis-

substituted perfluoroalkylthio oxetane. The prepolymer obtained was a white waxy solid, clearly not an elastomer. No characterization as to molecular weight, nature of the end groups, polydispersivity, equivalent weights, etc. of the the waxy solid was given. Absent such a characterization, it is unknown as to whether Falk et al.'s material may be further reacted with an isocyanate to produce a polyurethane polymer. No examples of the preparation of a polymer from any prepolymer is given.

Manser (U.S. Patent No. 4,393,199) teaches a method for polymerizing oxetane monomers by employing an initiator/catalyst system composed of an alkyl diol and a Lewis acid catalyst, BF_3 etherate. Manser teaches that not all oxetane monomers can be homopolymerized and that the rate of polymerization of bis-substituted oxetane monomers is dependent upon the nature of the substituent at the 3 position on the monomer. Manser does not teach or suggest the polymerization of mono-substituted fluorinated alkoxymethylene oxetanes to produce low viscosity, well defined, difunctional hydroxy-terminated assymetric prepolymers with fluorinated side-chains, nor does he suggest that the prepolymer derived from that polymerization could be cured with diisocyanates to obtain elastomers having exceedingly low surface energies.

Vakhlamova (Chem. Abst. 89:110440p) teaches synthesis of oxetane compounds substituted at the number 3 carbon of the oxetane with $-\text{CH}_2\text{O}-\text{CH}_2-\text{CF}_2-\text{CF}_2-\text{H}$ groups. The terminal alkyl portion of this substituent is thus: $-\text{CF}_2\text{CF}_2-\text{H}$ in which the terminal or omega carbon bears a hydrogen atom. As discussed supra, the Zisman and Pittman works shows that the presence of the hydrogen significantly increases the surface energy of the polymer derived from these monomers. Falk et al. (US 5,097,048) also recognizes that surface energy increases with the hydrogen atom on the terminal carbon by stating that "fluoroalkyl compounds which are terminally branched or contain omega-hydrogen atoms do not exhibit efficient oil repellency". Further, Vakhlamova focuses on the bis-substituted monomer as he hydrolyzes and polymerizes only the bis-substituted monomer.

A characteristic of the polymers formed from the

polymerization of the bis-substituted oxetanes of Falk et al., and the other proponents of bis-substituted oxetanes is that the resulting products are crystalline solids. The bis side-chains are highly ordered and symmetric. Consequently, they pack efficiently to form a crystalline structure. For example, a prepolymer prepared from 3,3-bis(chloromethyl)oxetane is a crystalline solid that melts in the neighborhood of 220 °C. This significantly affects the commercial use of these polymers as either or both mixing and elevated temperatures will be required in order to dissolve or melt the Falk et al. polymer for further polymerization or application.

Polymerization of the bis-substituted perfluorinated alkoxyethylene oxetanes has received little attention in the art. Moreover, the polymers derived from the bis-substituted perfluoroalkylthiol oxetanes are waxy solids and will not function as a soft segment in the preparation of commercially useful elastomers and coatings. Further, the ability of a bis-substituted oxetane monomer to homopolymerize appears to be dependent upon the nature of the side-chain at the 3 carbon with no assurance such polymerization will occur, the difficulty of polymerization apparently being due to the interference by the 3-carbon side-chains. Polymerization, and the products of polymerization, of the bis monomer accordingly are unpredictable and inconsistent.

Accordingly, there is a need in the art for a fluorinated elastomer product having low surface energies and the other properties enumerated above, and a production strategy therefor, beginning with a premonomer production process that is easy and inexpensive, to produce an asymmetrical mono-haloalkyl methyl oxetane premonomer, which upon further reaction produces an oxetane monomer having a single fluorinated side-chain, which mono-substituted fluorinated monomer is capable of homopolymerization and copolymerization to produce an essentially non-cross-linked soft segment, difunctional, linear, asymmetric prepolymer for further reaction to produce fluorinated elastomers and thermoset plastics, resins and coatings having hydrophobic properties, low surface energy, very low glass transition temperatures, low dielectric

constants, high abrasion resistance and tear strength, high adhesion and low refractive indices.

5

THE INVENTION

OBJECTS:

10 It is among the objects of this invention to provide fluorinated elastomers and thermoset plastics with fluorinated alkoxyethylene side-chains having good hydrophobic properties, low surface energies, very low glass transition temperatures, low dielectric constants, high abrasion resistance and tear strength, high adhesion and low refractive indices;

15 It is an object of this invention to provide a process for making and using fluorinated elastomers and thermoset plastics with fluorinated alkoxyethylene side-chains having low surface energies, very low glass transition temperatures, low dielectric constants, high abrasion resistance and tear strength, high adhesion and low refractive indices;

20 It is an object of this invention to provide fluorinated elastomers and thermoset plastics with fluorinated alkoxyethylene side-chains having good hydrophobic properties, low surface energies, very low glass transition temperatures, low dielectric constants, high abrasion resistance and tear strength, high adhesion and low refractive indices from the process of this invention;

25 It is another object of this invention to provide the compositions in which the fluorinated elastomers and plastics of this invention are used as fouling and ice release coatings, drag reduction coatings, moisture barrier coatings; catheters; artificial prosthesis components such as joints, hearts, and valves; contact lenses; intraocular lenses; films, paints; adhesives; non-transfer cosmetics; water repellent coatings; oil/stain resistant coatings; incendiary binders; lubricants, and the like; and processes for the production and use of such coatings, adhesives, binders and
35 compositions;

It is another object of this invention to provide a hydroxy terminated polyether prepolymer having asymmetric, alkoxymethylene side-chains with terminal perfluorinated alkyl groups for the production of the elastomers and thermoset plastics of this invention;

It is another object of this invention to provide a hydroxy terminated polyether co-prepolymer having asymmetric, mono-substituted fluorinated alkoxymethylene side-chains with terminal perfluorinated alkyl groups and a backbone composed of FOX monomer segments and of tetrahydrofuran (THF) segments for the production of the elastomers and thermoset plastics of this invention;

It is another object of this invention to provide the use of the prepolymers and co-prepolymers of this invention as, and as components, inter alia, in: coating compositions; lubricants; and pump oils which impart hydrophobic properties, low surface energies, low coefficient of friction, very low glass transition temperatures, low di-electric constants, high abrasion resistance and tear strength, high adhesion and low refractive indices to these resins, oils, lubricants and coatings;

It is another object of this invention to provide the process for the production of the hydroxy-terminated fluorinated polyether prepolymer having asymmetric, fluorinated alkoxymethylene side-chains of this invention;

It is another object of this invention to provide processes for the production of hydroxy-terminated fluorinated co-prepolymers having, fluorinated alkoxymethylene side-chains and a backbone composed of FOX monomer segments and THF segments;

It is another object of this invention to provide prepolymer and polymeric products of the processes of homopolymerization and of copolymerization of the FOX monomers of this invention;

It is another object of this invention to provide products of the processes of copolymerization of the FOX monomers of this invention with THF;

It is another object of this invention to provide FOX monomers derived from mono-haloalkyl 3-methyloxetanes, the monomers

being mono-substituted at the 3 carbon with a fluorinated alkoxyethylene side-chain for the production of the prepolymers of this invention, and processes for the production, use and polymerization thereof;

5 It is another object of this invention to provide the product of the processes for production of FOX monomers of this invention;

10 It is another object of this invention to provide processes for making FOX monomers derived from mono-haloalkyl-3-methyloxetanes, the FOX monomers being mono-substituted at the 3-carbon with a fluorinated alkoxyethylene side-chain for the production of the prepolymers of this invention;

15 It is another object of this invention to provide a relatively simple and inexpensive process for the production of 3-haloalkyl-3-methyloxetane as a premonomer for the FOX monomers of this invention;

It is another object of this invention to provide products from the processes for the production of 3-haloalkyl-3-methyloxetane as a premonomer of this invention; and

20 Still other objects of the invention will be evident from the Specification, drawings and claims hereof.

DICTIONARY

25 Aprotic Solvent: A solvent that does not donate a proton.

BrMMO: Acronym for 3-bromomethyl-3-methyl oxetane, the preferred premonomer of this invention.

30 Contact Angle: The obtuse or internal angle between the surface of a liquid and the surface of an object in contact with the liquid. A high contact angle corresponds to high hydrophobicity.

FOX

Copolymerization: Reaction of a FOX monomer with a either a different FOX monomer or a non-fluorinated monomer to produce a FOX co-prepolymer.

35 DSC: Acronym for differential scanning calorimeter, a

device used for determining a compounds glass transition temperature.

Elastomer: A polymeric material, such as rubber, which can be stretched under low stress to at least twice its original length and, upon immediate release of the stress, will return with force to its approximate original length.

FOX: Acronym for Fluorinated Oxetane. As used in the disclosure of this invention the term "FOX" is normally preceded by a number; e.g., 3-FOX, 7-FOX, etc. The numerical designation indicates the number of fluorine moieties on the single fluorinated side chain on the 3-carbon of the FOX monomer.

GLC: Acronym for gas-liquid chromatography. A device and method used as a separation technique to determine purity and percent conversion of starting materials.

GPC: Acronym for gel permeation chromatography. A device and method used to determine molecular weight.

HMMO: Acronym for 3-hydroxymethyl-3-methyloxetane, an intermediate in the production of the arylsulfonate oxetane premonomer.

FOX Homopolymerization: Reaction of a FOX monomer with itself to produce a FOX homo-prepolymer.

Hydrophobicity: The degree to which a substance lacks an affinity for, or repels, or fails to absorb water.

Lewis Acid A substance that can accept an electron pair from a base; thus AlCl₃ and BF₃ are Lewis acids.

Mono-substituted Oxetane: In the context of this invention, broadly a non-

bis substituted oxetane compound. More specifically, it refers to the 3-halomethyl-3-methyloxetane premonomers and FOX monomers of this invention where the 3-carbon of the oxetane ring is substituted with only one fluorinated side chain and the other 3-carbon side group is a non-fluorinated moiety; e.g., a methyl or ethyl group.

FOX Monomer: In the context of this invention, a mono-substituted fluorinated oxetane or FOX.

Phase Transfer Catalyst: Effectuates or mediates reactions in a dual-phase heterogeneous reaction mixture.

FOX Premonomer: Those 3-haloalkane-3-methyloxetane compounds which upon reaction with fluorinated alkoxides yields the FOX monomers of this invention.

FOX Prepolymer: A hydroxy terminated, polyether oligomer comprising from about 20 to about 300 FOX or FOX/THF monomer units which, upon reaction with a polyisocyanate will yield polyurethane elastomers.

Tetrahydrofuran: A commercially available 5-membered cyclic ether, abbreviated THF.

TME: Acronym for 1,1,1-tris(hydroxymethyl)ethane, the starting material for the BrMMO premonomer synthesis.

BRIEF DESCRIPTION OF DRAWINGS:

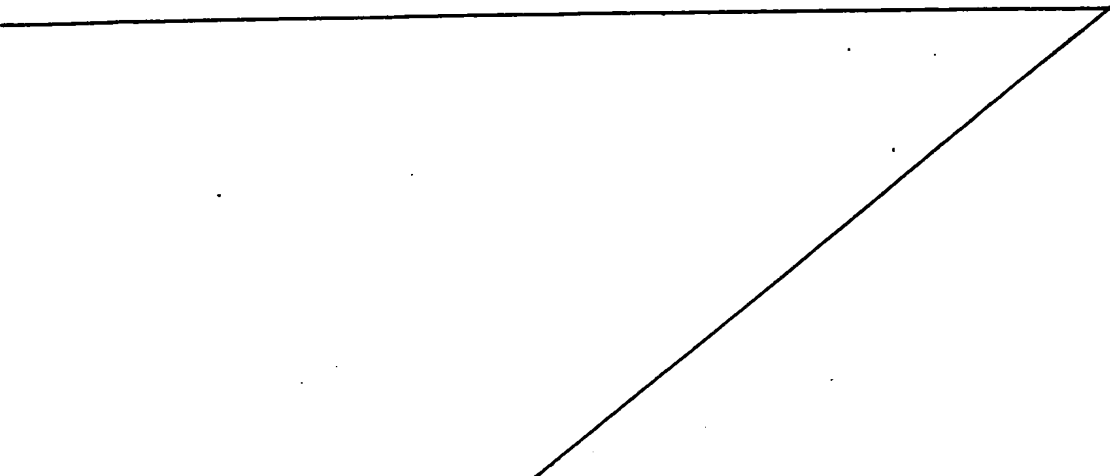
The invention is illustrated in part by reference to the drawings in which:

Fig. 1 is a photograph of contact angle of drops of water on a FOX polymer of this invention compared to a Teflon surface; and

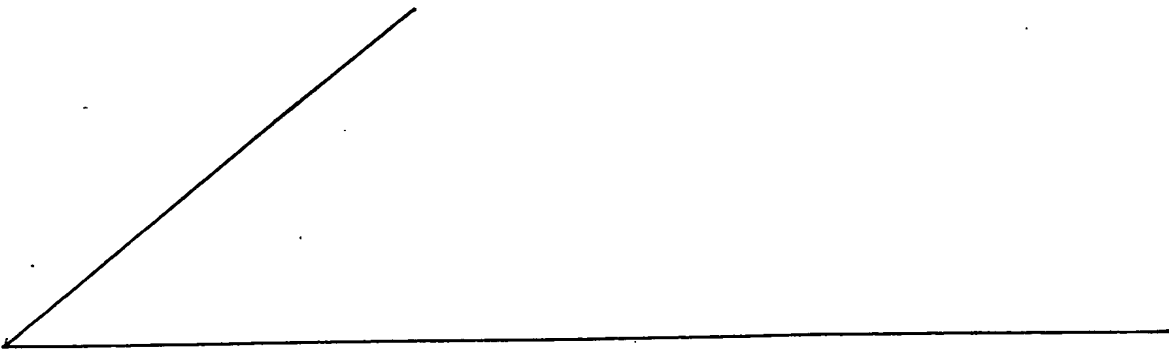
Fig. 2 is a summary of the polymerization reaction of FOX monomers by cationic ring opening reaction.

SUMMARY:

5 This invention is directed to mono-haloalkyl oxetane premonomers, mono-substituted oxetanes monomers having fluorinated alkoxymethylene side-chains derived from these premonomers, hydroxy-terminated prepolymers derived from these monomers, and polymers produced from these prepolymers, as well as the synthesis processes associated with each, and the use of the premonomers, monomers, prepolymers and ultimate polymers, both directly and as components of



- REMAINDER OF THIS PAGE INTENTIONALLY LEFT BLANK -



compositions. .

5 The premonomers, monomers, polyether hydroxy-terminated
prepolymers and resulting compositions thereof are particularly
useful for the preparation of polyurethane elastomers, thermoset
10 plastics and coatings which exhibit a wide variety of useful
properties including, inter alia, hydrophobic properties, low surface
energies, low glass transition temperatures, low dielectric
constants, high abrasion resistance and tear strength, low
coefficients of friction, high adhesion and low refractive indices.
15 A major application is for non-stick coatings, in that the adhesion
of the polymer of this invention is better than Teflon, the surface
energy is lower, the application is easier, and the applied film is
flexible with good abrasion resistance and tear strength permitting
application to both flexible and rigid surfaces. Examples are anti-
fouling coatings, ice release coatings, flexible optical fiber
cladding, conduit and aqueduct coatings or linings, surface coatings,
anti-graffiti coatings, automotive top-coat compositions (e.g., car
wax), particularly at low temperatures due to low glass transition
temperatures on the order of -40 to -50°C. The low index of
20 refraction and good oxygen permeability, coupled with the optical
clarity of some of the elastomers produced from the prepolymers make
them useful for contact lenses and intraocular lenses. Of course,
uses for elastomers are well known, and the improved properties of
the elastomers of this invention permit an even wider range of uses.

25 As noted above, we have discovered an improved route to
producing fluorinated elastomers. Our discovery includes an
improved, two-step process for the synthesis of a mono-substituted
haloalkyl oxetane premonomer which is easier and less expensive than
currently known processes. The premonomers in turn are used in
30 another novel process to produce mono-substituted fluoroalkyl
oxetanes (FOX monomers). Further, the process is so versatile, that
bis-fluoroalkyl oxetanes may be produced by this process in high
yields.

35 The monomers are used to produce homo- or co-prepolymers
characterized as non-cross linked, assymetrical, hydroxy-terminated,

linear oligomers having from about 10 to about 500 carbons, preferably 20 to about 200 carbons, i.e., FOX prepolymers. These prepolymers are crucial to the production of fluorinated elastomers in that they substantially retain their integrity in subsequent polymerizing reactions (e.g., reactions with diisocyanates or polyisocyanates) to provide the soft segment blocks of the resulting polymers which, in combination with the hard blocks formed during polymerization, produce good elastomers. While the background does not have any showing of homo- or co-polymerization of either the bis or the mono-substituted fluorinated alkoxymethylene oxetanes to produce prepolymers containing soft segment required for production of elastomers, the processes of our invention will readily polymerize both mono- and bis-substituted FOX monomers. The reaction mechanism of our process will produce prepolymers from bis fluoroalkyl oxetane monomers in high yields as well as from monosubstituted FOX monomers.

We have also discovered in the reactions and processes of the background that the presense of two, symmetric side chains, as in the bis-substituted oxetane monomers of Falk et al. result in slow reaction rates and lower yields. Without wishing to be bound by theory, we presently believe this is due to the presense of the two side groups of the bis-monomer compounds sterically hindering the initiation and the propagation reaction of the growing prepolymer chain. Whereas the background shows polymerization of just the thio-linked bis-oxetane monomer (and no ether-linked side-chains) such polymerization is difficult to initiate and when successful, results in a prepolymer that is crystalline. The resulting prepolymers are more symmetric and more regular than prepolymers produced from mono-substituted FOX monomers and, therefore, pack more efficiently to form crystalline materials.

Surprisingly, and contrary to the teachings of the prior art, two fluorinated side chains are not necessary to impart hydrophobic and low surface energy properties. The art teaches that the more fluorine, the better the properties, but did not recognize that the presense of two side chains leads to steric hindrance and formation of crystalline materials. In contrast, we believe the asymmetry

presented by the single (mono) group having fluorinated substituents of the FOX monomers of our invention which upon polymerization prevents the regularity in packing and results in amorphous prepolymers.

5 Unexpectedly, although the homo- and co-prepolymers composed of FOX monomers and of FOX/THF co-monomers contain less than half of the number of fluorine moieties as a bis-substituted prepolymer, they surprisingly produce polymers that have similar surface energies as a polymer derived from prepolymers having two fluorinated side-
10 chains. Further, even though the FOX/THF prepolymers of our invention contain less fluorine than the FOX prepolymers of our invention, the elastomers produced from the FOX/THF prepolymers surprisingly exhibit surface and physical properties comparable to the elastomers produced from the FOX prepolymers.

15 We have discovered a polymerization process which virtually eliminates the formation of undesirable by-products. The presence of non-functional or mono-functional materials in the prepolymers result in coatings with poor mechanical and surface properties. Consequently, these coatings have limited commercial value. Non-
20 functional materials, mainly cyclic tetramers and trimers, are formed during the ring opening polymerization from chain "back-biting". Monofunctional materials, on the other hand are formed due to counter-ion terminations, such as diethyl ether and fluoride ion terminations. The processes of this invention are unique in their
25 lack of by-product production. Production of cyclic tetramers and monofunctional prepolymers are almost undetectable.

30 1. Monomers

a) BrMMO Pre-monomer

 The FOX monomers of this invention are preferably derived from 3-bromomethyl-3-methyloxetane ("BrMMO"). While the preferred
35 leaving group on the mono-substituted haloalkyl oxetane is bromine,

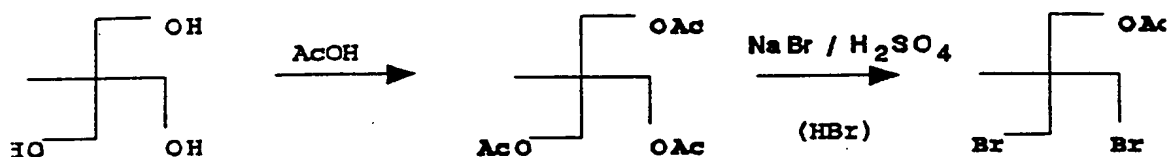
other halogens such as chlorine and iodine, as well as aryl sulfonates may be used. Reaction with BrMMO provides a convenient route in the preparation of 3,3-asymmetrically substituted oxetanes. BrMMO can be converted into a large variety of asymmetrical substituted oxetanes via SN_2 displacement with energetic groups such as nitro, nitrate, azido, amino, difluoroamino and nitroamino being introduced. Monomers for polymer radical cure coatings such as oxetanes substituted at the 3-position with vinyl, allyl, homoallyl and styryl groups can also be prepared.

As described in the background, the processes currently practiced for the production of 3-haloalkyl-3-methyl oxetanes, and more particularly to the production of BrMMO, are typified by low yields, side-reaction impurities, long, multi-step synthetic schemes and the use of expensive, toxic chemicals with hazardous materials and hazardous waste handling and disposal problems. These represent significant obstacles in the commercial scale-up of these processes. Consequently, 3-haloalkyl-3-methyl oxetane is not currently commercially available.

The process for the production of BrMMO of this invention, however, uses common inexpensive starting materials and provides BrMMO cleanly in high yields with only two steps. The process is novel in that it incorporates an *in-situ* generation of HBr. Unexpectedly, the *in-situ* generation of HBr permits the use of an alcohol with a molecular weight greater than n-butanol to produce a primary bromide in high yield with no by-products.

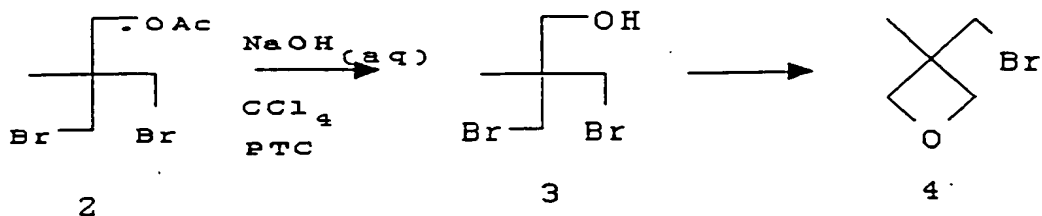
In the first step, as shown in Formula 1 below, 3-bromo-2-bromomethyl-2-methylpropyl acetate 2 (the dibromoacetate of 1,1,1-tris(hydroxymethyl)ethane or TME) is formed via bromination of the TME in glacial acetic acid with *in-situ* generated HBr. The HBr is formed *in situ* from the reaction of sulfuric acid with sodium bromide. Reaction temperature may range from about 100 to about 130°C, preferably about 120°C. We have discovered that the formation of the triacetate of TME unexpectedly more easily undergoes displacement with the bromide ion produced by the *in situ* generation of HBr. This step is novel in that this is the first time that a

primary alcohol (having a molecular weight greater than n-butanol) has been converted in high yield to a primary bromide using a sodium bromide/sulfuric acid process. Further, the in-situ formation of the HBr reagent significantly simplifies the reaction and the concomitant materials handling concerns of such a strong acid were it not so produced. Unexpectedly, the bromination of the TME tri-acetate only produces the TME dibromoacetate. Surprisingly, formation of the mono-bromo and tri-bromo TME derivatives is not observed.



Formula 1

In the second step, see Formula 2 below, the oxetane ring is closed by reacting the TME dibromoacetate with NaOH in refluxing CCl₄ (or n-butyl chloride) using a quaternary ammonium salt as a phase transfer catalyst (PTC). The ratio of the PTC to the TME dibromoacetate may range from 0.1 to about 2.0% wt/wt and is preferably 0.5% wt/wt. Upon reflux, the TME dibromo derivative 3 closes to produce the 3-bromomethyl-3-methyloxetane 4. Reaction temperature is dependent upon the reflux temperature and may range from room temperature to about 100°C, preferably from about 70 to about 80°C. An unexpected result of these reaction scheme is the absence of by-products from competing reactions.

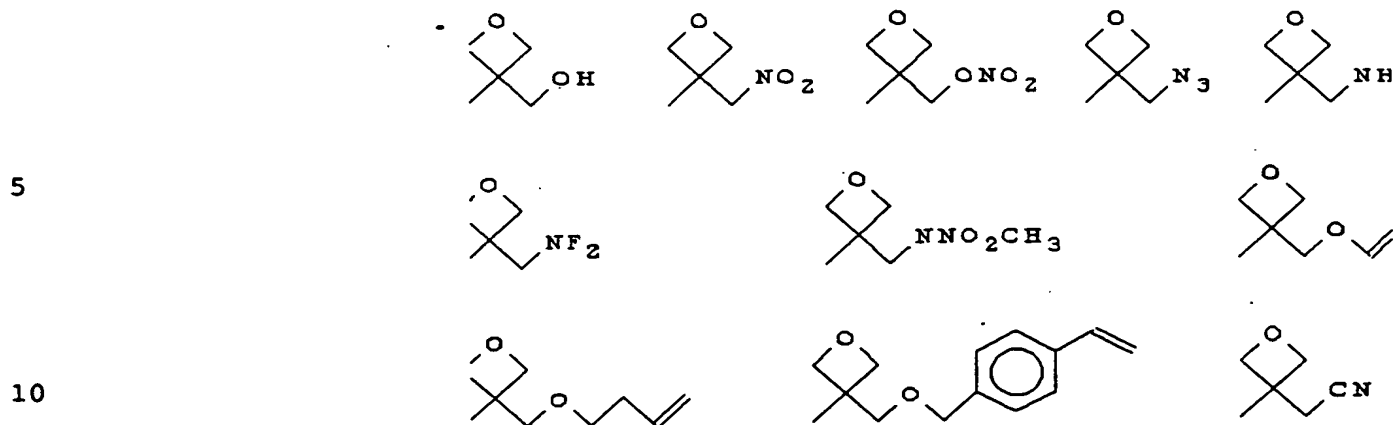


Formula 2

This phase transfer catalyzed intramolecular cyclization has not been attempted before for the production of BrMMO. Prior attempts have resulted in low yields of the cyclic products (12-60%) due to two principle side reactions. The first side reaction is a 1,4-elimination with the formation of a stable olefin in preference to the relatively more strained oxetane ring. A second competing reaction is the formation of the dimer and trimer.

These side reactions are minimized by choosing an appropriate solvent. We have found that n-butyl chloride and carbon tetrachloride provided yields of BrMMO on the order of 94-97%. Other solvents investigated, such as acetonitrile, toluene, DMF, ligroine, 1,1,2-trichloroethane, benzene, n-hexane and hexanes gave more complex reaction mixtures containing both competing side reactions of elimination and dimerization.

BrMMO can easily be converted to a large variety of asymmetrically substituted oxetanes via displacement of the primary bromide, an excellent leaving group. These monomers can then be polymerized via Lewis acids to provide polymers with a wide range of applications in energetic and coating materials. Examples of synthesized and possible monomers are listed below.



The ability to produce these monomers is dependent upon the clean, high yield process for the formation of BrMMO without the competing side reactions and associated by-products normally associated with this type of reaction. This is due to the unexpected effect of the phase transfer reaction of a base catalyzed internal cyclization of the TME dibromo derivative 3 of Formula 2.

While this discussion has been directed to the synthesis process of BrMMO, the reaction conditions described above can be used to produce a 3-bromomethyl-3-ethyl oxetane using 1,1,1-trimethylol propane ("TMP") as the starting material. Also, this process can be used for the synthesis of other mono-haloalkyl oxetanes such as 3-chloromethyl-3-methyloxetane, 3-iodomethyl-3-methyloxetane, 3-chloromethyl-3-ethyloxetane, etc.

OXETANE MONOMERS

The BrMMO of this invention may be further processed for the preparation of mono-substituted FOX monomers and prepolymers derived from the homo-polymerization and copolymerization of the FOX monomers.

The incorporation of fluorine in a polymer alters the properties of the resulting polymer:

1. Thermal stability increases thus extending the upper

use temperature of the polymer and allows these materials to be processed at higher temperatures without degradation making them suitable for use in environments where other hydrocarbon based polymers cannot be used.

5 2. Surface energy decreases thus improving the release characteristics of the polymer making it suitable for use as backings for adhesive tapes, release coatings for molds, fouling release coatings for ship hulls, and the like.

10 3. Refractive index of the resulting polymer is reduced making it useful for optical applications such as contact lenses, intraocular lenses, coatings for optical instruments, cladding for optical fibers, and the like.

15 4. Coefficient of friction is reduced thus improving the lubricity of the coating making it useful in applications such as vehicle seals, windshield wipers, drag reducing coatings for sail boats, airplanes, etc.

20 5. Hydrophobicity increases, thus improving water repellency and moisture barrier characteristics making the polymer useful for encapsulating electronic devices, moisture barrier films and coatings, rain erosion coatings, anti-corrosion coatings, etc.

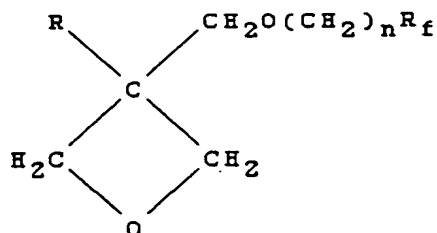
25 6. Oleophobicity increases, thus making the polymer oil repellent and useful as a stain resistant coating for garments and carpets.

30 7. Flammability decreases, thus improving flame retardancy, for example, on garments coated with the polymer.

8. Environmental stability of the polymer improves, thus making the polymer more stable when exposed to ultraviolet light and moisture.

The mono-substituted fluorinated alkyloxy-3-methyloxetane

monomers of this invention have the following formula:



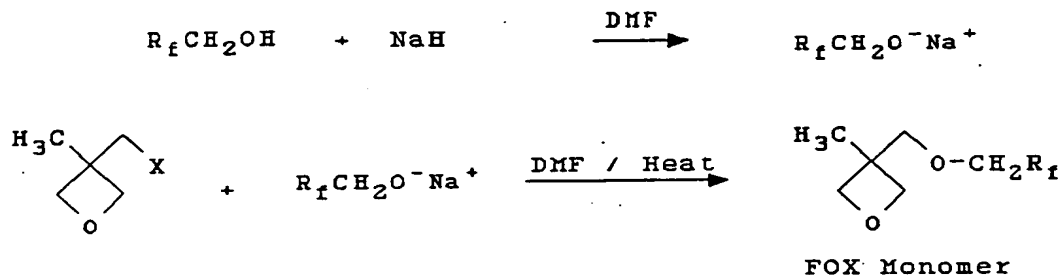
Where:

n is 1 to 3,

R is methyl or ethyl, and

R_f is a linear or branched chain fluorinated alkyl and isoalkyl having from 1 to 20 carbons, or an oxaperfluorinated polyether having from 4 to about 60 carbons.

The FOX monomers of this invention are obtained by reaction of aryl sulfonate derivatives of 3-hydroxymethyl-3-methyloxetanes (arylsulfonate-MO) or the reaction of mono-substituted 3-haloalkyl-3-methyloxetanes with fluorinated alkoxides in the presence of a polar aprotic solvent:



Examples of R_f:

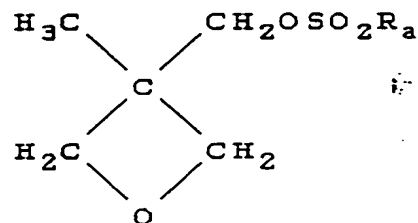


where: R_f is linear or branched chain perfluorinated alkyl or isoalkyl having from 1 to 20 carbons, or an oxaperfluorinated polyether having from 4 to about 60 carbons; and

$X = \text{Br, Cl, I or an aryl sulfonate.}$

Note that the numeric FOX designation is determined by the number of fluorine atoms in the terminal perfluoroalkyl group of the side-chain.

The aryl sulfonate derivatives of the hydroxyalkyl oxetanes have the general formula:



Where: R_a is monocyclic aryl having from C_6 to C_{10} carbons, e.g., benzyl, tolyl, xylyl, mesityl or an alkyl such as $-\text{CH}_3$ or $-\text{CF}_3$.

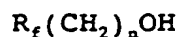
The preferred sulfonates are toluene sulfonates, e.g., p-toluene sulfonate derivatives of 3-hydroxymethyl-3-methyloxetane (HMMO).

The fluorinated alkoxides are obtained by the reaction of fluorinated alcohols with sodium hydride in a suitable solvent such as dimethylformamide:



Although sodium hydride is the preferred base for this reaction, other bases such as potassium hydride, potassium t-butoxide, calcium hydride, sodium hydroxide, potassium hydroxide, NaNH_2 , n-butyl lithium and lithium diisopropylamide may be used.

The fluorinated alcohols which can be used have the general formula:

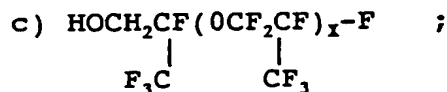
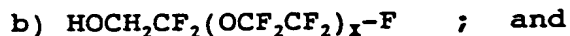
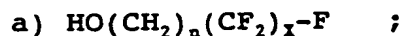


wherein:

n is 1 to 3; and

R_f is a linear or branched chain fluorinated alkyl or isoalkyl having from 1 to 20 carbons, or an oxaperfluorinated polyether having from 4 to about 60 carbons.

Examples of suitable fluorinated alcohols are: trifluoroethanol, heptafluorobutanol, pentadecafluorooctanol, tridecafluorooctanol, and the like. Other useful alcohols include fluorinated alcohols having the following formulas:



wherein n is 1 to about 3 and x is 1 to about 20.

Whereas the preferred solvent for the formation of the alkoxide from these alcohols is dimethylformamide (DMF), other solvents such as dimethylacetamide, DMSO and hexamethylene phosphoramidate (HMPA) may be used.

The pre-monomer of this invention, BrMMO, is particularly well suited for the synthesis of the oxetane monomers in that the BrMMO is uniquely clean and free of by-products resulting from its novel synthetic pathway. An example of the latter is the p-toluene sulfonate derivative of 3-hydroxymethyl-3-methyloxetane. A high yield of the oxetanes having pendant alkoxyethylene groups with terminal perfluorinated alkyl groups is obtained.

The displacement reaction can be conducted at temperatures

ranging from 25 °C - 150 °C, however, the preferred temperature is between 75 °C and 85 °C. At lower temperatures, the rate of displacement may be considered slow and marginally useful for commercial scale-up. At higher temperatures (> 120 °C), the rate of displacement is extremely fast. However, at these higher temperatures other side reactions such as hydrolysis of the premonomer to 3-hydroxymethyl-3-methyloxetane dominate. Thus, the preferred reaction temperature is < 120 °C.

Preferred Process for Synthesis of FOX Monomers

We have recently discovered a preferred process for preparing FOX monomers in high yields that eliminates the use of organic solvents and strong bases, such as NaH. The elimination of organic solvents reduces hazardous waste generation and air emissions of volatile organic compounds. The process steps are as follows:



where: R_f is linear or branched chain perfluorinated alkyl or isoalkyl having from 1 to 20 carbons, or an oxaperfluorinated polyether having from 4 to about 60 carbons; and
 $\text{X} = \text{Br}, \text{Cl} \text{ or } \text{I}.$

In this process, a mixture of 3-haloalky-3-methyloxetane, fluoroalcohol, a base such as sodium hydroxide or potassium hydroxide, and a phase transfer catalyst is heated in an aqueous

medium at 80-85 °C until GLC analysis reveals complete consumption of the starting materials. Upon completion of the reaction, the product is recovered by separation and distillation of the organic phase. The organic phase contains most of the FOX monomer. The recovered FOX monomer is polymer grade and has a purity normally in excess of 99%. Isolated yields are high and range from 80% to 90% for the purified FOX monomer. Yields prior to separation and purification exceed 90% for the crude product.

Although a variety of bases such as calcium hydroxide, magnesium hydroxide, tetrabutylammonium hydroxide, etc. can be used for this process, the preferred bases are sodium hydroxide and potassium hydroxide as they are readily available in large quantities and are relatively inexpensive.

Phase transfer catalysts function by transferring the counterion so that it is more soluble in the organic phase. A variety of phase transfer catalysts can be used for this process, such as tetramethylammonium bromide, tetraethylammonium bromide, tetramethylammonium iodide, cetyltributylammonium bromide, crown ethers, glycols, and the like. The preferred catalyst is tetrabutylammonium bromide due to its relatively low cost and good solubility in both organic and aqueous mediums.

The above reaction can be conducted at temperatures as low as 50°C and as high as 120°C. However, at low temperatures, the rate of displacement is extremely slow and competing side reactions such as hydrolysis start to dominate. At higher temperatures, the rate of displacement is extremely fast requiring specialized equipment that can handle pressure, thus making the process uneconomical and unattractive for commercial scale-up.

The above preferred phase transfer catalyst process is limited to the 3-haloalkyl-3-methyloxetanes and, therefore, precludes using the arylsulfonate derivatives of the 3-hydroxymethyl-3-methyloxetane as starting materials for the synthesis of FOX monomers. This is because arylsulfonates are sensitive towards hydrolysis and under the above phase transfer conditions, hydrolyze readily to form 3-hydroxymethyl-3-

methyloxetane, thus resulting in lower yields. This limitation is overcome, however, by the process of this invention which provides high purity 3-bromomethyl-3-methyloxetane in high yields.

2. Prepolymers

There are three types of prepolymers of this invention: Homo-prepolymers where the prepolymer is assembled from only one FOX monomer; Co-prepolymers where the prepolymer is assembled from a mixture of FOX monomers; and FOX/THF co-prepolymers where a FOX monomer (or mixture of FOX monomers) is copolymerized with tetrahydrofuran (THF).

One of the main applications of the hydroxy-terminated, FOX prepolymers is in the development of hydrophobic, non-stick, low friction materials. The most important criteria in preparation of these materials is the minimization of the surface energy, which is a measure of the wettability of the material and defines critical properties such as its hydrophobicity and adhesive characteristics.

In order to prepare materials with low surface energies, it is critical that the fluoroalkyl group is present in the side-chain and that the terminal carbon of the fluoroalkyl group is perfluorinated. The requirement to have fluorine in the side-chain rather than in the polymer backbone is demonstrated by comparing the surface energies of fluorinated polyacrylates and polytetrafluoroethylene (Teflon). Surface energy of Teflon, which contains fluorine in the polymer backbone, is 18.5 ergs/cm². By comparison, the surface energy of polyfluoroacrylates, which contains fluorine in the side-chains, is between 10-12 ergs/cm². Also, fluoroalkyl groups that contain hydrogen or halogen (Cl, Br, I) on the terminal carbon have considerably higher surface energies than those with CF₃ groups. The dependence of surface energy on the surface constitution of typical organic materials is shown in Table 1.

TABLE 1
SURFACE ENERGIES OF ORGANIC MATERIALS

SURFACE CONSTITUTION	ERGS/CM ² @ 20 °C
-CF ₃ Close Packed	6
-CF ₂ H	15
-CF ₂ -	18
-CH ₃	22
-CH ₂ -	31
-CH ₂ CHCl-	39
Polyester	43

It is also preferred to use oxetane monomers substituted at the 3-position with only one perfluoroalkyl group since polymerization of 3,3'-disubstituted oxetane monomers yield prepolymers that are largely crystalline which foreclose preparation of elastomers having the required preproperties. For example, polymerization of 3,3'-bis(chloromethyl)oxetane yields a crystalline polymer that melts at approximately 220°C. Similarly, polymerization of 3,3'-bis(ethoxymethyl)oxetane provides a prepolymer that melts at approximately 80°C.

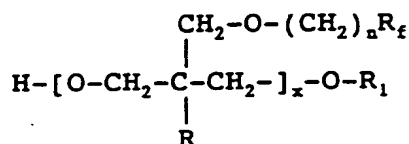
It should be noted that crystalline prepolymers can not be used in the preparation of polyurethane elastomers. Also, prepolymers from disubstituted FOX monomers contain large amounts of nonfunctional cyclic oligomers, which degrade polymer properties. Surface properties are dependent on the amount of fluorine at the polymer/air interface, and in the case of FOX prepolymers, excellent enrichment of the polymer surface with fluorine is achieved and yet with only one perfluoroalkyl group. Surprisingly, we have discovered that a second fluorinated side chain does not significantly enhance the surface properties, and

thus, its introduction in the prepolymer is both not cost effective and forecloses the the fluorinated elastomer field since it introduces crystalline symmetry properties.

5 We have discovered and recognized that placing the fluorine in the side-chain, rather than on the backbone as in Teflon, improves surface lubricity, and the resulting prepolymer/elastomer exhibits a surface energy lower than a polymer having fluorine in just the backbone. We have discovered, however, that there is a trade-off between having the fluorine on the side-chain versus on 10 the backbone: While we get increased lubricity by incorporating a fluorinated side-chain, there is a reduced thermal stability as compared to a polymer having fluorine only on the backbone, for example Teflon.

15 Hydroxy Terminated Homo- and Co-prepolymers

The invention also comprises the process of polymerizing FOX monomers, as well as the resultant hydroxy-terminated prepolymers. These prepolymers have the following formula:



wherein:

n is 1 to 3;

R is methyl or ethyl;

R₁ is H or a terminal alkyl alcohol residue having from about 2 to about 5 carbons;

R_f is a linear or branched chain fluorinated alkyl or isoalkyl having from 1 to 20 carbons, or an oxaperfluorinated polyether having from 4 to about 60 carbons; and

x is 10 to about 250.

The method of making the FOX homo- and co-prepolymers includes the steps of:

- 1) charging a reactor with a catalyst, an initiator and a solvent;
- 2) adding a solution of FOX monomer(s) in an appropriate organic solvent at a temperature between -20°C and +60°C;
- 3) reacting the FOX monomer(s) with the catalyst/initiator solution;
- 4) quenching the reaction; and
- 5) separating the FOX prepolymer by precipitation in methanol.

The polymerization can be homopolymerization or copolymerization in which a mixture of two or more of the afore-described oxetane monomers is added to the polymerization zone. A particularly useful copolymerization is block polymerization in which the comonomers are sequentially added in selected proportions to obtain block copolymers of controlled block sizes and properties.

Solution polymerization of the invention may be conducted at a solids concentration of 5%-85%, however the preferred polymerization is normally conducted at a concentration of 50-60% solids. The polymerization is conducted in the presence of a suitable inert solvent, preferably a halogenated C₁ to C₅ hydrocarbon, e.g., methylene chloride, carbon tetrachloride, chloroform, trichloroethylene, chlorobenzene, ethyl bromide, dichloroethane, fluorinated solvents, etc. with the preferred solvent being methylene chloride, or a mixture of methylene chloride and Freon. Other solvents such as sulfur dioxide, hexanes, petroleum ether, toluene, dioxane and xylene can also be used.

The FOX monomers readily polymerize in the presence of a Lewis acid catalyst (i.e., compounds capable of accepting a pair of electrons) and a polyhydroxy aliphatic compound as a polymerization initiator. Suitable Lewis acids for use as catalysts include: complexes of boron trifluoride, phosphorus pentafluoride, antimony pentafluoride, zinc chloride, aluminum bromide, and the like. The preferred Lewis acid catalyst is a BF₃•THF complex.

Suitable initiators are polyhydroxy aliphatic compounds such as alkyl and isoalkyl polyols having from 2 to about 5 carbons and from 2 to 4 hydroxyls, e.g., ethylene glycol, butane-1,4-diol, propylene glycol, isobutane-1,3-diol, pentane-1,5-diol, pentaerythritol, trimethylolpropane, and the like, with the preferred initiator being butane-1,4-diol.

The catalyst and initiator are preferably mixed for 5-10 minutes in the solvent prior to the addition of the FOX monomers. The ratio of catalyst to initiator ranges from 1:1 to 1:5 mol/mol with the preferred ratio being 1:1 to 1:2 mol/mol. An example of a preferred catalyst, initiator and solvent combination is boron trifluoride tetrahydrofuranate, butane-1,4-diol and methylene chloride. The ratio of the monomer to the catalyst ranges from about 10:1 mol/mol to about 300:1 mol/mol, with the preferred range about 50:1 to 100:1 mol/mol.

In a typical example, the catalyst and the initiator are mixed in a solvent prior to the addition of the FOX monomer(s). As oxetane monomers possess relatively high strain energy and undergo exothermic, ring-opening polymerizations, the FOX monomer(s) is added slowly over a period of time to control the reaction temperature and to avoid run-away reactions. The progress of the reaction is monitored by ^1H NMR and when >95% of FOX monomer is consumed, the reaction is quenched with water. The prepolymer is purified by precipitation in methanol.

The molecular weight of the prepolymer can be controlled by varying the monomer/catalyst ratio and the reaction temperature. Generally, lower monomer/catalyst ratios and higher reaction temperatures favor the formation of lower molecular weight prepolymers. The ratio of monomer to catalyst can be from 10:1 to 300:1, however, the ratios commonly used range from 50:1 to 100:1 monomer/catalyst.

The reaction temperature can be varied from -20°C to $+60^\circ\text{C}$, however, the preferred reaction temperature is $+5^\circ\text{C}$. At higher temperatures, formation of monofunctional materials, mainly $-\text{CH}_2\text{F}$ terminated materials, is observed. Mono-functional materials can act

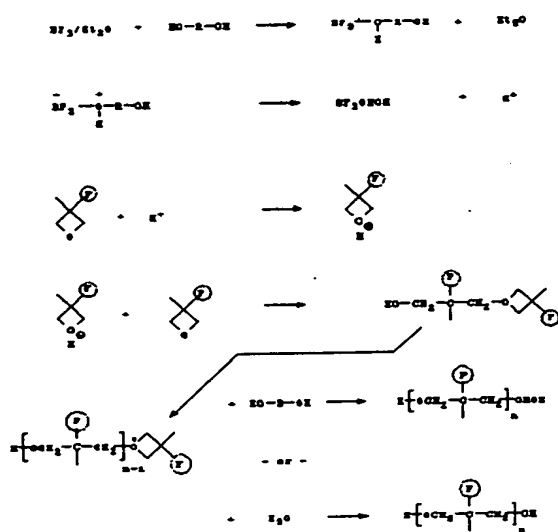
as chain terminators, thus limiting the molecular weight of the final polymer as well as increasing the polydispersivity. This, in turn, results in polymers having poor mechanical and physical properties.

Cyclic oligomers are normally formed as by-products in the synthesis of polyether prepolymers. These materials are non-functional and reduce the usefulness of the prepolymers. Moreover, these materials can leach out of the polymer matrix, and thereby drastically affect the surface and mechanical properties of the polymer. Prepolymers prepared by homopolymerization of FOX monomers contain approximately 2-7% cyclic tetramer.

The BF_3 -etherate catalyst results in approximately 10%-15% of the mono-functional material and approximately 6%-7% cyclic tetramer by-product.

The preferred catalyst is $\text{BF}_3 \cdot \text{THF}$ which results in less than 2% of the cyclic tetramer byproduct and eliminates the formation of the mono-functional prepolymer. In turn, this increases the functionality of the prepolymer and leads to polymers having excellent mechanical, surface and physical properties.

The polymerization of FOX monomers occurs by cationic ring-opening reaction. The mechanism for which is presented below:



See Fig. 2.

The polymerization is initiated by the proton donated by the initiator, and the protonated oxetane ring undergoes propagation with other oxetanes to generate the polymer chain. The growing polymer chain is then terminated either with alcohol or water to give hydroxy-terminated polyether prepolymers of this invention. It should be noted that the prepolymers of this invention are mixtures of prepolymers resulting from both alcohol and water terminations.

We have discovered through NMR analysis ($^1\text{H}/^{13}\text{C}$) of the prepolymer that the initiator fragment, in particular the butanediol fragment, is located at the end of the polymer chain, and is not incorporated in the middle of the prepolymer backbone. The NMR data ($^1\text{H}/^{13}\text{C}$) clearly shows the presence of a $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ group which can only occur if the butanediol fragment is present at the end of the prepolymer chain. If the butanediol fragment was incorporated in the middle of the prepolymer, we would see only two peaks corresponding to the symmetrical $-\text{OCH}_2\text{CH}_2-\text{CH}_2\text{CH}_2\text{O}-$ group. Our NMR data does not show the presence of this group. While in theory the initiator fragment may be incorporated in the middle of the prepolymer, it is highly unlikely that the bulky, high molecular weight prepolymer will compete efficiently as a chain terminator with a low molecular weight, highly mobile butanediol. The result of the polymerization with the diol initiator is a prepolymer with an unsymmetrical butanediol fraction at the end of the prepolymer chain. Our work is consistent with Conjeevaram et al. (J. of Polymer Science, Vol. 23, 429-444 (1985)) in which 1,4-butanediol is used as an initiator in conjunction with a $\text{BF}_3 \cdot \text{etherate}$ to polymerize un-substituted oxetanes. His ^{13}C NMR analysis also reveals incorporation of the butanediol fragment as the unsymmetrical group $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ at the end of the polymer chain.

The prepolymers of this invention are amorphous, low viscosity oils that are easy to process. The inherent viscosity of the prepolymers are between 0.05 and 0.08 dL/g. The number average molecular weights of the prepolymers as determined by gel permeation chromatography, are between 1,000 and 30,000. The polydispersivity,

a measure of the spread or "Q" of the molecular distribution, is very low, on the order of less than 5 and typically between 1.1-2.0. The prepolymers exhibited unimodal molecular weight distribution, and were contaminated with approximately 2-7% cyclic tetramer.

5 It should be noted that molecular weights reported in this invention are expressed relative to well characterized polystyrene standards. The equivalent weight of the prepolymers was determined by ^1H NMR employing TFAA end group analysis and were between 2,500 and 9,000. The glass transition temperature of the prepolymers, as
10 determined by DSC analysis, was between -38°C and -45°C .

The structural analysis of the homo- and co-prepolymers of this invention was conducted with ^1H , ^{13}C and ^{19}F NMR spectroscopy. ^1H NMR analysis revealed the presence of a trimethyleneoxide-based polyether backbone. ^1H NMR analysis also indicated that when
15 $\text{BF}_3 \cdot \text{etherate}$ is used as a catalyst, substantial amounts of mono-functional material with $-\text{CH}_2\text{F}$ and $-\text{OCH}_2\text{CH}_3$ end-groups is formed. However, when $\text{BF}_3 \cdot \text{THF}$ is used as a catalyst, formation of mono-functional material is not observed. ^1H NMR was also used to
20 establish the ratio of the two monomers in the co-prepolymer and the identity of the end groups. ^{19}F NMR analysis confirmed the presence of fluoroalkyl side-chains and the absence of materials with $-\text{CH}_2\text{F}$ end groups and impurities such as Freon, HF and BF_3 catalyst.

^{13}C NMR analysis of the co-prepolymers such as poly 3/7-FOX and poly 3/15-FOX, revealed that these materials are random
25 copolymers with little, if any, block structure.

The prepolymers described above are oils that can be used as lubricants or as additives for a variety of applications. For example, these materials can be used as additives in cosmetics to impart water repellency and release characteristics. Also, these
30 materials can be used as additives in engine oils to reduce engine wear and improve performance. The principal application, however, is in the preparation of fluorinated polymers which in turn can be used for diverse applications ranging from car wax to materials for medical and dental applications such as prosthetics and catheter
35 linings.

Co-Prepolymers With Tetrahydrofuran

We have discovered that the fluorinated oxetanes of this invention may be co-polymerized with THF to provide a FOX/THF coprepolymer having very unique, unexpected characteristics. These are a new class of fluorine containing, hydroxy-terminated, polyether prepolymers, which when cured with polyisocyanates, provide tough polyurethane elastomers that are characterized by low glass transition temperatures and low surface energies. Moreover, these elastomers can be incorporated into coatings that exhibit high abrasion resistance and low coefficient of friction. Combinations of these properties make polymers derived from these fluorinated coprepolymers extremely attractive for a variety of applications including, but not limited to, anti-fouling (release) coatings; ice release coatings; corrosion resistant coatings, automotive top coats (e.g., car wax), windshield wipers; belt strips; and various household goods; seals and gaskets; encapsulants for electronic devices; oil and dirt resistance coatings; and numerous medical/dental applications.

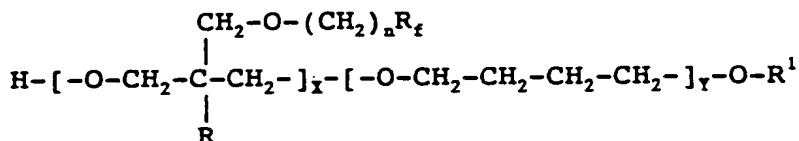
Tetrahydrofuran (THF) is a five membered cyclic ether that is commercially available and is known to polymerize or copolymerize with cationic catalysts but not with anionic catalysts. Attempts to copolymerize THF with cyclic ethers, in particular, oxetanes is unpredictable. Polymerization occurs but the products are often not random copolymers. Due to the vast differences in ring-opening polymerizability between THF and oxetanes, it is more likely that the product is a block copolymer rather than a random copolymer. Poly THF (PTHF) is a semi-crystalline polymer that melts at ca. 50°C, and when employed as the soft segment in urethane elastomers, is likely to crystallize at low temperatures, causing problems with physical properties such as poor flexibility, incomplete or little recovery after elongation, poor modulus, and the like. In a block, or non-random, copolymer, similar problems can occur since THF blocks can crystallize and form semi-crystalline polymers.

In the FOX/THF random coprepolymer of this invention, THF and

oxetane segments are randomly spaced along the polymer backbone, thus leading to products that are amorphous oils. The random nature of our co-prepolymers prevents backbone tacticity or any other form of regularity that lends itself to ordering and the development of crystallinity. Hydroxy-terminated polyether prepolymers that are low in crystallinity, preferably amorphous, are particularly suitable as the soft segments for urethane elastomers.

In this invention we describe the copolymerization of FOX monomers with tetrahydrofuran to give FOX/THF coprepolymers. Copolymerization of FOX monomers with THF, not only reduces the cost of fluorinated prepolymers by using less of the relatively more expensive FOX monomers, but also provides prepolymers with superior properties. The co-prepolymers of this invention are random copolymers and are ideal as soft segments for urethane elastomers. Moreover, these FOX/THF coprepolymers are amorphous oils that are easy to process. Also, the use of THF as a coreactant allows the polymerization to be conducted in bulk and eliminates the use of ozone depleting solvents such as Freons.

The FOX co-prepolymer composition has the following general structure:



where: n is 1-3;

R is methyl or ethyl;

R_f is a linear or branched perfluorinated alkyl group having 1-20 carbons, or an oxaperfluorinated polyether having from about 4-20 carbons;

X is 1-100 and Y is 10-150; and

R¹ is H or an alkyl alcohol residue having from about 2 to 5 carbons.

and: M_n is 2,000 to 50,000; and